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OF WEAR METALS IN
USED LUBRICATING OILS

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Dwight. E. Veinot

December 1980

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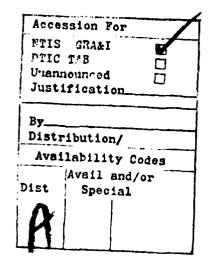
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ABSTRACT

An x-ray fluorescence spectrometric technique was developed for the direct determination of iron and copper wear metal concentrations in used lubricating oils from CH 124 "Sea King" helicopter engines. The x-ray fluorescence wear metal levels were compared to the atomic absorption wear metal levels determined on corresponding samples. In general, the x-ray fluorescence results indicated higher levels of wear metal contamination and also provided earlier indications of abnormal wear based on more pronounced changes in detected wear metal production than did the results obtained by atomic absorption analysis.

RESUME

On a mis au point une technique de spectrométrie par
fluorescence des rayons X pour déterminer directement les
concentrations de poussières de fer et de cuivre dans les
huiles usées des moteurs des hélicoptères CH 124 "Sea King".
On a comparé les valeurs obtenues à l'aide de cette méthode
avec celles obtenues par absorption atomique sur des
échantillons correspondants. En général, les résultats
obtenus par fluorescence des rayons X montraient des
concentrations plus élevées de poussières métalliques
contaminantes et permettraient de déceler plus tôt que
l'analyse par absorption atomique une usure anormale d'après
le changement plus marqué des quantités de poussières
métalliques produites.

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NOTATION

SOAP	Spectrometric Oil Analysis Program
AAS	Atomic Absorption Spectrometric
XRFS	X-ray Fluorescence Spectrometric
$^{\circ}C$	degrees centigrade
ml	millilitre
cps	counts per second
ppm	parts per million
Fe	iron
Cu	copper
KV	kilovolt
ma	milliamp

1. INTRODUCTION

The Canadian Forces machinery health monitoring program is based on relating the internal condition of a machine to the concentration of various wear metals in used lubricating oil from the machine[1]. At present, the Canadian Forces Spectrometric Oil Analysis Program (SOAP), utilizes atomic absorption spectrometric (AAS) techniques for determining wear metal levels in the used oils. The basic concept on which the program operates is that moving contact between oil lubricated metallic components is accompanied by friction which causes a transformation of the contacting surfaces into small particles (wear particles) which are deposited in the lubricating oil. The rate of increase in the production of these wear particles is an important indicator of the internal condition of the machine. It is used together with established guideline maximum wear metal levels in predicting incipient failure and the need for machinery overhaul; the object being to avoid catastrophic failure in service.

Although the AAS method of wear metal analysis has proven itself to be effective over many years of use, it suffers from the inherent drawback that in order to be detected, the wear metals must be dissolved in the used oil or present as finely divided particles. The probability that a wear metal particle will be detected decreases as the particle size increases, mainly because of two effects. Firstly, particles are not aspirated into the flame as efficiently as metals in solution and secondly, the flame may not have sufficient energy to atomize the particles. It is commonly accepted that particles greater than 5 micrometers in size escape detection. However, during the critical stages of abnormal wear, it is characteristic that both the quantity and size of the wear particles produced increase. Therefore, a potentially valuable source of information regarding internal condition during the most critical stages of wear is lost to the analyst. A further complication to the AAS method results from the requirement to reduce sample viscosity in order to achieve efficient aspiration of the sample into the flame by diluting with a low viscosity solvent. This is an important step in the analytical procedure which requires substantial attention and time to avoid sample preparation errors. Also, because of the equipment required for AAS analysis, the technique offers no potential for development as an on-line analysis technique.

It follows then, that a method which could be used to analyze the samples as received or could be adapted for

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on-line analysis and which would be less sensitive to the size of wear particles than the AAS method, would offer the possibilities of both earlier and more positive indication of impending failure and would also reduce the possibility of errors resulting from sample preparation procedures.

This report describes an x-ray fluorescence spectrometric (XRFS) procedure that can be used to analyze used lubricating oils as received with increased probability of wear detection due to its ability to detect both metals in solution and particles of all sizes. The procedure has been used to measure iron and copper wear metal levels in used oils from CH 124 "Sea King" helicopter engines. The results obtained have been compared to the AAS results obtained on the same samples in order to evaluate the diagnostic capabilities offered by the XRFS method relative to those offered by the AAS method.

Iron and copper were chosen to illustrate the XRFS oil analysis procedure for several reasons. Iron and/or copper are the principle alloying elements in the majority of oil lubricated components in the T58-GE-8F engines. Therefore, accurate determination of the concentrations of these two elements in the used oil provides an effective means of condition monitoring. However, other elements such as silver, chromium, nickel, aluminum and magnesium have also been used effectively for condition monitoring by the AAS method. The XRFS procedure described does not provide adequate sensitivity for the determination of magnesium and aluminum. To do these elements at 1 ppm sensitivity requires analysis within a vacuum or helium filled chamber. Silver, chromium and nickel are seldom present at greater than 1 ppm but the procedure described could be employed to determine these elements if they were present at concentrations greater than 1 ppm. Lower level detection i.e., 0.1 ppm of these elements (especially silver) by a modified XRFS technique will be the subject of future work.

2. EQUIPMENT

A Philips PW 1410 manual/vacuum x-ray spectrometer equipped with a Philips PW 2182 rhodium side window x-ray tube was used for this work. The rhodium x-ray tube was powered by a Philips PW 1130 x-ray generator. Fluorescent x-rays from elements in the liquid oil samples were detected sequentially using tandemly operated scintillation and flow proportional counters. Ten percent methane in argon was used in the flow proportional detector. The x-ray processing equipment used

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included a Philips PW 4280 amplifier analyzer, PW 1362 ratemeter, PW 4234 scaler and a PW 4260 timer.

3. PROCEDURE

The used lubricating oil samples were warmed to 70°C and shaken vigorously to ensure homogeneous distribution of the wear debris in the sample. Approximately a 10 ml portion of each sample was poured into a disposable plastic sample cup (Chemplex Industries, Cat. No. 1540) which was fitted with a thin (4 micrometer) polyester film (Somar Laboratories Inc., Cat. No. 3615-33) bottom window. A similar polyester window was then fitted to the top of the sample cup to eliminate spills when handling the samples.

The analysis conditions were optimized for both iron and copper based on a calculation of the figure of merit as described by Jenkins[2] using results obtained from a 100 ppm metal-in-oil standard. Calibration curves of x-ray response versus iron and copper wear metal concentrations were prepared using standards containing 0, 5, 10, 20, 50, 100, 200 and 500 ppm of each metal in synthetic MIL-L-23699B lubricating oil. During the analysis, the samples were spun at a rate of one revolution per second to minimize the effect of surface irregularities. Figure I shows the calibration curves from 0 to 500 ppm. The concentrations obtained by XRFS for iron and copper wear metal levels were compared to the iron and copper wear metal levels that were determined by the normal AAS procedure in corresponding samples. The absolute concentrations of iron and copper in the oil samples were determined by ashing weighed aliquots of each sample, dissolving the ash in acid and then determining the metal concentrations in the resulting aqueous solutions.

4. RESULTS AND DISCUSSION

X-ray response was linearly dependent on concentrations up to at least 500 ppm with a lower limit of detection of 1 ppm for both copper and iron. Figure I shows the calibration curves used for this work. The relatively high background levels shown in these curves are the result of high scattering of exitation source x-rays by the oil.

Table I shows a comparison of the XRFS and the AAS iron and copper wear metal levels found in successive samples of used oil from T58-GE-8F helicopter engines that were

considered to be operating normally. As shown by the four
cases presented in Table I, both the AAS and XRFS results
indicate low wear metal levels with negligible change in the
concentrations determined in successive samples. Thus both
techniques indicate normal operation. Note that in cases 2
and 3 the iron and copper concentrations obtained by XRFS
analysis are higher than those obtained by the AAS analysis.
Absolute concentrations of these metals, obtained by ashing
a weighed aliquot of each sample, dissolving the ash in acid
and determining iron and copper concentrations in the resulting
aqueous solutions, validated the results obtained by XRFS
analysis in all cases.

Table II shows a comparison of the XRFS and AAS wear
metal levels found in successive samples of used oil from
T58-GE-8F engines that were considered to be operating
abnormally or that had failed. In all cases, the XRFS results
show higher levels of wear metal contamination than the AAS
results. In addition, they indicate a rising concentration
at least one sample interval earlier than the AAS results and
show, at the same time, a more pronounced and therefore more
readily noticeable deviation from the levels indicative of
normal wear. For example, referring to case 7, the AAS results
indicate a stablized iron concentration of 3 ppm, thus
indicating normal operation. However, the XRFS results indicate
a change in status with associated increased iron concentrations
from the sample taken at 80.4 hours onwards until the engine
was finally removed from service because large particles were
discovered on the filter elements. The sample taken at 155.0
operating hours was not representative, probably because of a
sampling error. Other cases shown in Table II also show the
earlier and more evident failure prediction capability of XRFS
wear metal analysis. The XRFS results obtained on these cases
were also validated by the ashing procedure previously described.

5. CONCLUSIONS

The XRFS oil analysis procedure offers a simple and
accurate means of determining copper and iron wear metal
concentrations in used lubricating oils. Unlike the convention-
ally employed AAS method, this method provides accurate analytical
results independent of the size of the wear particles. A
comparison of the XRFS and AAS results indicates that for
normally operating engines, both sets of results show close
agreement. However, for abnormally operating engines the XRFS
results show higher wear metal levels and a more pronounced
change in concentration in successive samples. Thus the XRFS

procedure provides an earlier and more positive indication of
impending failure. The XRFS results were found to be more
accurate than the AAS results especially when contamination
levels were high. In addition, the XRFS method does not
require that the samples be diluted with low viscosity solvents
thus eliminating one potential source of error and reducing
sample preparation time. One additional advantage of the XRFS
method is that with the appropriate equipment modifications,
the basic concept could be applied to on-line analysis of the
oil during service.

REFERENCES

1. C-05-005-008/AM-000, Aerospace Spectrometric Oil Analysis Program, 79-09-28.

2. Jenkins, Ron, An Introduction to X-Ray Spectrometry, Heydon and Son Ltd., 1974.

TABLE I

WEAR METAL LEVELS IN USED OIL

FROM NORMALLY OPERATING ENGINES

Case Number	Equipment Serial Number	Hours Since Oil Change	A.A.S.		X.R.F.S.	
			Fe (ppm)	Cu (ppm)	Fe (ppm)	Cu (ppm)
1	275115	6.0	<1	<1	<1	<1
		9.1	<1	<1	<1	<1
		11.4	<1	<1	<1	<1
		11.9	<1	<1	<1	<1
		42.2	<1	<1	<1	<1
		69.3	1	<1	<1	<1
2	275071	0.5	<1	<1	1	4
		3.2	<1	<1	1	4
		32.6	<1	<1	1	4
3	275006	7.0	<1	<1	2	3
		33.1	<1	<1	3	4
		57.7	<1	<1	3	4
		81.9	<1	<1	3	4
4	275169	28.8	0	<1	<1	<1
		52.8	0	<1	<1	<1
		86.9	0	<1	<1	<1
		111.6	0	<1	<1	<1

TABLE II

WEAR METAL LEVELS IN USED OILS

FROM ABNORMALLY OPERATING ENGINES

Case Number	Equipment Serial Number	Hours Since Oil Change	A.A.S.		X.R.F.S.	
			Fe (ppm)	Cu (ppm)	Fe (ppm)	Cu (ppm)
1	275100	24.1	0	<1	2	3
		53.7	0	<1	4	3
		79.3	4	<1	9	3
		105.5	5	<1	9	3
2	275055	17.1	3	<1	7	4
		45.0	3	<1	13	4
	Failed	56.8	4	<1	330	62
3	275041	113.6	2	<1	8	3
		129.3	2	<1	8	3
		142.4	1	<1	8	3
		150.9	2	1	19	4
	particles on filter	150.9	2	<1	19	4
4	275119	99.6	1	<1	7	2
		111.9	2	<1	8	2
		126.6	2	2	17	2
		139.8	8	2	34	7
		147.9	8	2	42	7

(...Cont'd)

Case Number	Serial Number	Hours Since Oil Change	A.A.S.		X.R.F.S.	
			Fe (ppm)	Cu (ppm)	Fe (ppm)	Cu (ppm)
5	275170	12.3	1	<1	20	1
		24.4	1	<1	20	1
		39.3	2	<1	35	1
		54.7	2	<1	45	2
		70.0	2	<1	50	2
		82.5	2	<1	85	2
		95.9	3	<1	115	3
		108.6	4	<1	192	3
6	275035	2.8	1	<1	5	2
		16.9	3	<1	10	2
		30.9	6	<1	14	2
		43.9	11	<1	28	2
		55.6	10	<1	35	2
		61.4	12	<1	62	2
		64.1	16	<1	85	3
		65.1	19	<1	125	3
		65.6	19	<1	130	3
7	275151	80.4	2	<1	14	<1
		106.3	2	<1	26	<1
		121.1	3	<1	31	<1
		155.0	<1	<1	<1	<1
		176.6	3	<1	72	<1
		202.2	3	<1	76	<1
		208.2	3	<1	134	<1

Figure 1: Calibration curves for copper and iron in MIL-L-23699B lubricating oil.

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